Method for Applying Manganese Phosphate Layers

The invention relates to a method for applying manganese
phosphate layers to iron or steel surfaces using

5 phosphating solutions containing manganese, phosphate,
iron(II) ions as well as nitroguanidine, as well as its
application to workpieces that are subjected to sliding
friction.

10 On account of their high mechanical resistance, manganese
phosphate layers have proved ideal for various
applications, e.g. in order to reduce the friction of metal
surfaces sliding on one another or to facilitate the cold
forming of metals. However, relatively thick, coarsely

15 crystalline layers were obtained with the manganese
phosphate solutions that were initially commonly used,
these layers being particularly disadvantageous if fine
mechanical parts are to be treated. Numerous proposals
have therefore been made with the object of producing thin,

20 finely crystalline manganese phosphate layers. For
example, it is known that an improvement in the phosphate
layer can be obtained by adding condensed phosphates.
Phosphating solutions based on manganese phosphate are
however generally employed at high temperatures, which

25 means that, as a result of the considerable hydrolysis that
takes place at high temperatures, the effectiveness of the
condensed phosphates rapidly falls and/or replenishment
condensed phosphate has to be constantly added.

30 Another way of obtaining fine-grain phosphate layers is
described in German Auslegeschrift 1109 484. Nitrate-
containing phosphate solutions in which the amount of
nitrate is in excess of the amount of phosphate are used
for this purpose. The solutions should have a ratio of

35 nitrate to phosphate of about 1.5-4.5 : 1. It has been

found however that in many cases the intended effect is not achieved.

Furthermore, a method is known in which an increased amount
5   of free acid in the phosphating solution is specifically
employed in order to obtain particularly thin layers (DE-C-
1246356). However, on account of their low surface density
these layers can, in practice, only apply to special cases.

10   Finally it is known to add to a phosphating solution based
on manganese phosphate or manganese-iron phosphate in which
the concentrations with respect to manganese, iron(II),
phosphate and nitrate ions lie within specific limits,
proportionally more free P_2O_5 in relation to the total P_2O_5
15   than corresponds to the phosphating equilibrium in the
working phosphating solution. The aforementioned measure
is said to have the advantages of achieving a significant
decrease in the amount of slurry formed in the phosphating
and a reduction of the chemicals needed to produce a
20   specific amount of coating (DE-B-22 13781).

A common feature of the known methods is that manganese
phosphate layers are formed having significant roughness
depths. The reason for this is that the etching action in
25   manganese phosphate systems is already pronounced at the
start of the process and leads to a punctiform removal of
metal after an extremely short action time. On the other
hand, the layer formation takes place relatively slowly
compared with zinc phosphate systems. The pronounced
30   etching action and delayed layer formation can be observed
visually by a large evolution of gas over a relatively long
period, the so-called gas time.

The object of the invention is to provide a method that
35   leads to manganese phosphate layers having as low a

roughness depth as possible, but whose layer thickness is in the medium to high range.

This object is achieved by the method of the type mentioned in the introduction and corresponding to the invention in which, in order to produce a manganese phosphate layer having a minimum thickness of 2.5 μm and an averaged maximum roughness depth (R_z) of 2.5 μm, measured after drying, the workpieces are brought into contact with a phosphating solution containing

> 0.2 to 4 g/l of iron(II) ions
> 10 to 25 g/l of manganese ions
> 25 to 50 g/l of phosphate ions (calc. as P_2O_5)
> 3 to 35 g/l of nitrate ions
> 0.5 to 5 g/l of nitroguanidine

that has 7 to 24 points of free acid, 50 to 140 points of total acid, as well as an S value of 0.2 to 1.

The averaged roughness depth is defined according to DIN 4768, Sheet 1, and represents the arithmetic mean of the individual roughness depths of five mutually adjoining individual measurement stretches of identical length, defined as

$$R_z = 0.2 (Z_1 + Z_2 + Z_3 + Z_4 + Z_5)$$

The required maximum value of 2.5 μm refers only to the roughness depth of the manganese phosphate layer and disregards the depth of the untreated metal surface.

The aforementioned total point number is determined in a manner known *per se* by titrating 10 ml of the phosphating solution after dilution with water to about 50 ml using

phenolphthalein as indicator, until the colour changes from
colourless to red. The amount of 0.1 N sodium hydroxide
solution used represents the total point number. Other
suitable indicators for the titration are thymolphthalein
5 and ortho-cresolphthalein.

The free acid points are determined in a similar way,
dimethyl yellow being used as indicator and the titration
being carried out until the colour changes from pink to
10 yellow. Interfering metal ions are removed beforehand by
adding hexacyanoferrate (II) or hexacyanocobaltate (III)
ions. The S value is defined as the ratio of free P_2O_5 to
total P_2O_5. (For further details see W. Rausch, "Die
Phosphatierung von Metallen", Eugen G. Leuze Verlag,
15 Stuttgart 1974, pp. 273 ff.).

More particularly, it is known from GB-A-510684 to produce
manganese phosphate layers using phosphating solutions that
may also contain nitroguanidine in addition to numerous
20 other oxidising agents. However, it can be calculated from
the data relating to the point numbers of free acid and
total acid that the phosphating solutions contain
considerably lower concentrations of phosphating-active
components and - corresponding to the objective pursued in
25 the known method of improving the corrosion resistance of
metals - can form layers of a very low layer weight. The
patent specification does not contain any kind of
information on the roughness depth of the phosphate layer.

30 The investigations carried out on the development of the
present invention have shown that when using nitrate as
accelerator, which autocatalytically forms nitrite as a
result of the normally used high phosphating temperatures,
or when using nitrite or chlorate, the layer formation is
35 disturbed because of the deficient iron(II) content, or

layers are formed having only a very low layer weight or very low layer thickness. In contrast the use of nitroguanidine allows the iron(II) concentration to be kept below specific limits without resulting in an undesirable

5 sharp drop in the iron(II) content necessary for the formation of a qualitatively high-grade layer.

In order to assist the oxidation of iron(II), oxygen-containing gas, for example compressed air, may be blown

10 into the phosphating solution. Substances that oxidise iron(II), preferably potassium permanganate, may also be added. It should however be borne in mind that the iron(II) concentration should in no case fall below 0.2 g/l, since otherwise the desired layer weight will not

15 be obtained.

A preferred embodiment of the invention envisages bringing the workpieces into contact with a phosphating solution that contains 0.5 to 2 g/l of nitroguanidine. Reasons of

20 cost in particular are decisive in this connection.

Furthermore it is advantageous to adjust the concentration of iron(II) ions in the phosphating solution to a maximum concentration of 2.5 g/l. In this way, finely crystalline

25 layers of small roughness depth can also reliably be formed in the case of workpieces that are difficult to phosphate.

If workpieces with steel surfaces are to be phosphated, a further advantageous embodiment of the invention envisages

30 adding complex-forming agents to the phosphating solution in order to complex the alloying constituents of the steel. In particular chromium is such an alloying constituent. Suitable complex-forming agents are for example tartaric acid, but, in particular, citric acid. The constituents of

the steel that might adversely affect the layer quality are trapped by the addition of complex-forming agents.

A further advantageous modification of the invention
5 consists in bringing the workpieces into contact with a phosphating solution that additionally contains

        0.2 to 4 g/l of nickel ions

or

10   0.2 to 4 g/l of magnesium ions.

These additions produce an homogenisation of the etching attack on the metal surface to be treated and thereby achieve a stronger adhesion of the phosphate layer. Also
15 the appearance of the phosphate layer is improved as a result of the generally desirable dark coloration. In addition, the content of magnesium ions reduces the overall consumption of chemicals.

20 Finally, it is expedient to contact the workpieces with a phosphating solution in which at least a proportion of the manganese ions have been replaced by manganese carbonate in order to neutralise the free acid.

25 The contact of the workpieces with the phosphating solution preferably takes place at a temperature in the range from 75° to 95°C.

The workpieces may be brought into contact with the
30 phosphating solution in any appropriate way, preferably by immersion treatment. Treatment times of, in general, 1 to 15 minutes are appropriate.

As a rule it is necessary to clean the workpieces before
35 the phosphating. Acidic, neutral or alkaline cleaning

agents are used for this purpose. In general the
workpieces are thoroughly rinsed with water between the
cleaning and the phosphating of the workpieces.
Particularly after treatment with alkalis and acids, the
5   workpieces should be pre-rinsed in an aqueous slurry of
finely divided manganese phosphate in order to promote the
formation of particularly uniform finely crystalline layers
in the subsequent phosphating.

10   Phosphate layers having a layer weight of in general 5 to
30 g/m² can be obtained by means of the method according to
the invention.

The phosphate layers produced by the invention may, in a
15   manner known as *per se,* be lacquered or provided with
plastics coatings. In conjunction with corrosion prevention
oils, these measures serve to increase the resistance to
rust. The main application of the method according to the
invention however is in the treatment of workpieces that
20   are exposed to sliding friction. Such workpieces include,
for example, axles, gear mechanism parts and pistons of
internal combustion engines and compressors.

It is possible by means of the method according to the
25   invention, to produce manganese phosphate layers with
average to high layer thicknesses that, nevertheless, have
only a very low averaged roughness depth. The roughness
depth is ca. 30 to 50% below the values that were hitherto
normally obtained. As a result of the low roughness depth
30   the frictional resistance is considerably reduced for
workpieces that are subjected to sliding friction. The
reduction of the so-called gas time to about half the
hitherto usual time indicates that the duration of the
etching attack of the phosphating solution, and thus the
35   removal of metal from the workpiece, is considerably

reduced. It is assumed that the content of nitroguanidine
in the phosphating solution leads to a certain passivation
of the metal surface, which however permits a reduced
etching attack and/or leads to an earlier start of the
5   layer formation.

The invention is described in more detail with the aid of
the following example.

10   Example:

Steel cup-shaped tappets were first of all degreased by
immersion in a strongly alkaline, aqueous cleansing agent,
next rinsed with water, then pre-rinsed in a slurry of
15   finely divided manganese phosphate, and finally phosphated
by immersion in a phosphating solution at 80°C for a
duration of ten minutes.

The phosphating solution contained
20

       11.8   g/l of manganese,
        0.5   g/l of nickel,
       1   g/l of iron(II),
      36   g/l of phosphate (calculated as P_2O_5)
25   4.6   g/l of nitrate and
      0.36 g/l of citrate (calculated as citric acid).

The total point number of the phosphating solution was 80,
and the point number of the free acid was 11 (measured with
30   60 g of concentrate per 1 l of water). For the
determination of the total acid point number and free acid
point number, reference should be made to the details given
above.

183 g of a concentrate containing 6.45 wt.% of manganese, 0.28 wt.% of nickel, 0.05 wt.% of iron(II), 19.8 wt.% of P_2O_5, 2.5 wt.% of nitrate and 0.2 wt.% of citric acid, which was made up to one litre with fully deionised water, served

5 as the phosphating solution batch.

Finely crystalline phosphate layers with a layer weight of 7 g/m², corresponding to a layer thickness of 3 to 4 μm, and an averaged roughness depth R_z of 1.3 to 2.4 μm, were

10 obtained.   The gas time was 2 to 3 minutes.

A comparative test was carried out under identical conditions with the above phosphating solution, which however did not contain nitroguanidine.   Phosphate layers

15 were formed which, although being finely crystalline, nevertheless had an averaged roughness depth R_z of 5 to 6 μm.   The layer weight was 6 g/m².   The gas time was 6 to 10 minutes.